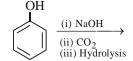
Chapter

# Alcohols, Phenols and Ethers

### Type A : Multiple Choice Questions

The product obtained from the reaction is:

[1998]



- (a) Benzene
- Toluene
- (c) Salicylic acid
- Benzoic acid
- Picric acid is: 2.

[2000]

- (a) Trinitrophenol (c) Trinitrobenzene
- Trinitrotoluene (d) Tribromobenzene
- 3. Lucas reagent is:

[2000]

- (a) anhy. AlCl<sub>3</sub> + conc. HCl
- (b) anhy. AlCl<sub>3</sub> + conc. HNO<sub>3</sub>
- (c) anhy. ZnCl<sub>2</sub>
- (d) anhy. ZnCl<sub>2</sub> + conc. HCl
- Lucas test is used for the detection of [2002]
  - (a) alcohols
- (b) alkyl halides
- (c) phenols
- (d) aldehydes
- 5. Intermolecular hydrogen bonding is strongest in: [2003]
  - (a) Methylamine
- (b) Phenol
- (c) Formaldehyde
- (d) Methanol
- Propan-1-ol can be prepared from propene by:

- (a)  $H_2O/H_2SO_4$
- (b)  $Hg(OAc)_2/H_2O$  followed by  $NaBH_4$
- (c)  $B_2H_6$  followed by  $H_2O_2$
- (d)  $CH_3CO_2H/H_2SO_4$
- 7. Among the following the one which reacts most readily with ethanol is [2004]
  - (a) p-nitrobenzyl bromide
  - (b) p-chlorobenzyl bromide
  - (c) p-methoxybenzyl bromide
  - (d) p-methylbenzyl bromide
- The most suitable reagent for the conversion of  $RCH_2OH \longrightarrow RCHO$  is: [2004]

- (a) KMnO<sub>4</sub>
- (b)  $K_2Cr_2O_7$
- (c) CrO<sub>3</sub>
- (d) PCC (pyridine chlorochromate)
- The major product formed in the following reaction is: [2005]

$$\begin{array}{c}
CH_{3} \\
CH_{3} - C - CH_{2}Br \xrightarrow{CH_{3}O^{-}} \\
H \\
CH_{3}
\end{array}$$

(a) 
$$CH_3$$
— $\stackrel{|}{C}$ — $CH_2OCH_3$ 

(b) 
$$CH_3$$
— $CH$ — $CH_2CH_3$   
 $OCH_3$ 

(c) 
$$CH_3 \stackrel{|}{-} CH_2$$
  
 $CH_3 \stackrel{|}{-} CH_3$ 

(d) 
$$CH_3 - \overset{\circ}{C} - CH_3$$
  
 $OCH_3$ 

The major product obtained on the monobromination (with Br<sub>2</sub>/FeBr<sub>3</sub>) of the following compound A is: [2006]

$$\bigcup_{A}^{OCH_3}_{CH_3}$$

(a) 
$$CH_3$$
 (b)  $CH_3$   $CH_3$ 

(c) 
$$OCH_3$$
  $OCH_3$   $OCH_3$   $OCH_3$   $OCH_3$   $OCH_3$ 

- 11. CH<sub>3</sub>OC<sub>2</sub>H<sub>5</sub> and (CH<sub>3</sub>)<sub>3</sub> C OCH<sub>3</sub> are treated with hydroiodic acid. The fragments obtained after reactions are [2007]
  - (a)  $CH_3I + HOC_2H_5$ ;  $(CH_3)_3CI + HOCH_3$
  - (b)  $CH_3OH + C_2H_5I; (CH_3)_3CI + HOCH_3$
  - (c)  $CH_3OH + C_2H_5I; (CH_3)_3COH + CH_3I$
  - (d)  $CH_3I + HOC_2H_5$ ;  $CH_3I + (CH_3)_3$  COH.
- **12.** In which of the following reactions the product obtained is *t*-butyl methyl ether? [2008]

(a) 
$$CH_3OH + HO - CH_2 - CH_3 \xrightarrow{conc.H_2SO_4} CH_3$$

(b) 
$$CH_3 - \overset{|}{C} - Br + CH_3OH \xrightarrow{HO^-Na^+} CH_3$$

(c) 
$$CH_3Br + Na^+O^- - \stackrel{\mid}{C} - CH_3 \longrightarrow CH_3$$

(d) 
$$CH_3 - O^-Na^+ + CH_3 - C^- - Br \longrightarrow CH_3$$

- **13.** Which of the following is a primary halide?
  - (a) Iso-propyl iodide

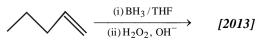
[2008]

- (b) Secondary butyl iodide
- (c) Tertiary butyl bromide
- (d) Neohexyl chloride
- **14.** An organic compound X on treatment with pyridinium chlorochromate in dichloromethane gives compound Y. Compound Y reacts with I<sub>2</sub> and alkali to form triiodomethane. The compound 'X' is [2008]
  - (a) C<sub>2</sub>H<sub>5</sub>OH
- (b) CH<sub>2</sub>CHO
- (c) CH<sub>3</sub>COCH<sub>3</sub>
- (d) CH<sub>3</sub>COOH
- **15.** The formation of diethyl ether from ethanol is based on: [2009]
  - (a) Dehydrogenation reaction
  - (b) Hydrogenation reaction
  - (c) Dehydration reaction
  - (d) Heterolytic fission reaction
- **16.** Chloropicrin is obtained by the reaction of
  - (a) steam on carbon tetrachloride [2010]
  - (b) nitric acid on chlorobenzene
  - (c) chlorine on picric acid
  - (d) nitric acid on chloroform

- **17.** Ethanol can be prepared more easily by which reaction? [2011]
  - (i)  $CH_3CH_2Br + H_2O \longrightarrow CH_3CH_2OH$
  - (ii)  $CH_3CH_2Br + Ag_2O$  (in boiling water)

—→ CH<sub>3</sub>CH<sub>2</sub>OH

- (a) by (i) reaction
- (b) by (ii) reaction
- (c) Both reactions proceed at same rate
- (d) by none
- **18.** An aromatic ether is not cleaved by HI even at 525 K. The compound is [2012]
  - (a) C<sub>6</sub>H<sub>5</sub>OCH<sub>3</sub>
- (b)  $C_6H_5OC_6H_5$
- (c)  $C_6H_5OC_3H_7$
- (d) Tetrahydrofuran
- **19.** The product of the following reaction is



- (a) 1-Pentanol
- (b) 2-Pentanol
- (c) Pentane
- (d) 1,2-Pentanediol
- 20. Ethanol when reacted with PCl<sub>5</sub> gives A, POCl<sub>3</sub> and HCl. A reacts with silver nitrite to form B (major product) and AgCl. A and B respectively are
  - (a)  $C_2H_5Cl$  and  $C_2H_5OC_2H_5$

[2013]

- (b)  $C_2H_6$  and  $C_2H_5OC_2H_5$
- (c)  $C_2H_5Cl$  and  $C_2H_5NO_2$
- (d)  $C_2H_6$  and  $C_2H_5NO_2$
- 21. Polyvinylalcohol can be prepared by [2013]
  - (a) polymerization of vinyl alcohol
  - (b) alkaline hydrolysis of polyvinyl acetate
  - (c) polymerization of acetylene
  - (d) reaction of acetylene with H<sub>2</sub>SO<sub>4</sub> in presence of HgSO<sub>4</sub>
- **22.** Compound 'A' of molecular formula C<sub>4</sub>H<sub>10</sub>O on treatment with Lucas reagent at room temperature gives compound 'B'. When compound 'B' is heated with alcoholic KOH, it gives isobutene. Compound 'A' and 'B' are respectively [2014]
  - (a) 2-methyl-2-propanol and 2-methyl-2-chloropropane
  - (b) 2-methyl-1 -propanol and 1-chloro-2-methylpropane
  - (c) 2-methyl-1 -propanol and 2-methyl-2-chloropropane
  - (d) butan-2-ol and 2-chlorobutane

#### c-154

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- 23. Which of the following alcohols gives the best yield of dialkyl ether on being heated with a trace of sulphuric acid? [2014]
  - (a) 2-Pentanol
  - (b) Cyclopentanol
  - (c) 2-Methyl-2-butanol
  - (d) 1-Pentanol
- **24.** Which of the following reagents convert propene to 1-propanol? [2015]
  - (a)  $H_2O, H_2SO_4$
  - (b) Aqueous KOH
  - (c) MgSO<sub>4</sub>, NaBH<sub>4</sub>/H<sub>2</sub>O
  - (d)  $B_2H_6, H_2O_2, OH^-$
- **25.** Which of the following fact(s) explain(s) as to why *p*-nitrophenol is more acidic than phenol?
  - I. –I Effect of nitro group.

[2015]

- II. Greater resonance effect of p-nitrophenoxy group
- III. Steric effect of bulky nitro group
- (a) I and II
- (b) I and III
- (c) II and III
- (d) II alone
- **26.** CICH<sub>2</sub>CH<sub>2</sub>OH is stronger acid than CH<sub>3</sub>CH<sub>2</sub>OH because of: [2016]
  - (a) I effect of Cl increases negative charge on O atom of alcohol
  - (b) I effect of Cl disperses negative charge on O atom to produce more stable cation
  - (c) I effect of Cl disperses negative charge on O atom to produce more stable anion
  - (d) None of these
- **27.** The ether that undergoes electrophilic substitution reactions is [2017]
  - (a) CH<sub>3</sub>OC<sub>2</sub>H<sub>5</sub>
- (b)  $C_6H_5OCH_3$
- (c) CH<sub>3</sub>OCH<sub>3</sub>
- (d)  $C_2H_5OC_2H_5$
- **28.** A triglyceride can have how many different acyl groups? [2017]
  - (a) 3
- (b) 2
- (c) 1
- (d) 4
- 29. In the reaction

Phenol  $\xrightarrow{\text{NaOH}}$  (A)  $\xrightarrow{\text{CO}_2+\text{HCl}}$  (B), here B is [2017]

- (a) benzaldehyde
- (b) chlorobenzene
- (c) benzoic acid
- (d) salicylic acid

- **30.** In the Victor-Meyer's test, the colour given by  $1^{\circ}$ ,  $2^{\circ}$  and  $3^{\circ}$  alcohols are respectively. [2017]
  - (a) red, colourless, blue
  - (b) red, blue, colourless
  - (c) blue, red, violet
  - (d) red, blue, violet

#### TYPE B: ASSERTION REASON QUESTIONS

**Directions for (Qs. 31-35):** These questions consist of two statements, each printed as Assertion and Reason. While answering these questions, you are required to choose any one of the following five responses.

- (a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
- (b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
- (c) If the Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- (e) If the Assertion is incorrect but the Reason is correct.
- **31. Assertion :** Resorcinol turns FeCl<sub>3</sub> solution purple. **Reason :** Resorcinol have phenolic group.

[2000]

- **32. Assertion :** Phenol is a strong acid than ethanol. **Reason :** Groups with +M effect decreases acidity at *p*-position. [2002]
- **33. Assertion:** Benzyl bromide when kept in acetone water, it produces benzyl alcohol.

**Reason :** The reaction follows  $S_N^2$  mechanism. [2003]

**34. Assertion :** The major products formed by heating C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>OCH<sub>3</sub> with HI are C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>I and CH<sub>3</sub>OH.

**Reason :** Benzyl cation is more stable than methyl cation. [2004]

**35. Assertion :** The ease of dehydration of the following alcohols is

**Reason :** Alcohols leading to conjugated alkenes are dehydrated to a greater extent. [2008]

**Directions for (Qs.36-40):** Each of these questions contains an Assertion followed by Reason. Read them carefully and answer the question on the basis of following options. You have to select the one that best describes the two statements.

- (a) If both Assertion and Reason are correct and Reason is the correct explanation of Assertion.
- (b) If both Assertion and Reason are correct, but Reason is not the correct explanation of Assertion.
- (c) If Assertion is correct but Reason is incorrect.
- (d) If both the Assertion and Reason are incorrect.
- **36. Assertion:** Phenyl is used as a household germicide.

**Reason :** Phenyl is phenol derivative and phenol is an effective germicide. [2010]

- **37. Assertion :** *ter*-Butyl methyl ether is not prepared by the reaction of *ter*-butyl bromide with sodium methoxide.
  - **Reason :** Sodium methoxide is a strong nucleophile. [2010]
- **38. Assertion :** Ethers behave as bases in the presence of mineral acids.
  - **Reason :** Due to the presence of lone pairs of electrons on oxygen. [2013]
- **39. Assertion :** Phenol undergo Kolbe reaction, ethanol does not. *[2014, 2015]* **Reason :** Phenoxide ion is more basic than
  - **Reason :** Phenoxide ion is more basic than ethoxide ion.
- **40. Assertion :** Ethyl phenyl ether on reaction with HBr form phenol and ethyl bromide.
  - **Reason :** Cleavage of C–O bond takes place on ethyl-oxygen bond due to the more stable phenyl-oxygen bond. [2016]

# **HINTS & SOLUTIONS**

# Type A: Multiple Choice Questions

2. (c) OH OH COONa
$$\xrightarrow{\text{NaOH}} \xrightarrow{\text{COO}}$$

$$\xrightarrow{\text{hydrolysis}}$$
Salicylic acid

Picric acid is sym-trinitrophenol 4.

$$O_2N \longrightarrow NO_2$$

$$NO_2$$

- Lucas reagent is anhydrous ZnCl<sub>2</sub> + HCl 5. which is used to distinguish between primary, secondary and tertiary alcohols.
- 6. (a) Lucas test is used for the determination of primary, secondary and tertiary alcohols.
- 7. Hydrogen bonding is formed in compounds in which H is attached to highly electronegative element like F, O and N.

- (ii) N is less electronegative than O, so H bond formed by amines will be weak than that by alcohols.
- (iii) C<sub>6</sub>H<sub>5</sub>OH forms weak H-bonding due to steric hinderance due to bulky phenyl group.

**8.** (c) 
$$CH_3CH = CH_2 \xrightarrow{B_2H_6} (CH_3CH_2CH_2)_3B$$

$$\xrightarrow{\text{H}_2\text{O}_2/\text{OH}^-} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$$
Propanol

9. Among the given compounds,

the first one can give carbonium ion most readily because the carbonium ion will be stabilised due to presence of NO2 group on the ring.

- 10. (d) The most suitable reagent for converting alcohol to acetaldehyde is PCC. Other reagent will convert alcohol to acid.
- 11. (d) The reaction is an example of  $S_N 1$  reaction

$$\begin{array}{c} \operatorname{CH_3} & \operatorname{CH_3} \\ \operatorname{CH_3} - \operatorname{CH} - \operatorname{CH_2Br} \xrightarrow{-\operatorname{Br}^-} \operatorname{CH_3} - \operatorname{CH} - \operatorname{CH} - \operatorname{CH}_2 \\ \operatorname{1^\circ carbocation} \end{array}$$

- **12.** The reaction is an example of electrophilic aromatic substitution. Although both OCH<sub>3</sub> and CH<sub>3</sub> groups are o,p-directing, the OCH<sub>3</sub> group dominates. Product (b) is favoured because the new coming group (Br) experiences least hindrance.
- In case of unsymmetrical ethers, the site of 13. cleavage depends on the nature of alkyl

e.g. 
$$CH_3 - O - C_2H_5 + HI$$
  $\frac{373}{4}$   $\frac{373}{4}$   $\frac{1}{4}$   $\frac{1}{8}$   $CH_3I + C_2H_5OH$  The alkyl halide is formed from the smaller

alkyl group.

However, in case of tertiary alkyl ether following reaction occurs.

$$CH_3 - OC(CH_3)_3 + HI$$
  $3/4$ 

 $({\rm CH_3})_3{\rm C-I+CH_3OH}$  The alkyl halide is formed from the tertiary alkyl group and the cleavage of such ethers occurs by  ${\rm S_NI}$  mechanism as the product is controlled by the formation of more stable intermediate tertiary carbocation from protonated ether.

- 14. (c) It is *Williamson's synthesis*. It involves the nucleophilic attack of *alkoxide ion* on alkyl halide according to S<sub>N</sub>2 mechanism. In order to prepare methyl tertiary butyl ether, we must use methyl halide (primary) and sodium tertiary butoxide, but not sodium ethoxide and *t*-alkyl halide because the latter undergoes elimination reaction rather than substitution.
- **15.** (d) Writing the structures, we get

(a) 
$$CH_3 - \overset{I}{C} - H$$
, Isopropyl iodide (2°)  $CH_3$ 

$$\begin{array}{ccccc} H & H & H \\ & & | & | & | \\ (b) \, H - C - C - C & C & -I \ , \textit{sec} - Butyl \ iodide \ (2^\circ) \\ & & | & | & | \\ & H & H & CH_3 \end{array}$$

$$CH_3$$
(c)  $H_3C-C-I$ , tert-Butyl iodide (3°)
 $CH_3$ 

$$\begin{array}{c} {\rm CH_3\,H} \\ ({\rm d})\,\,{\rm CH_3-CH_2-} \stackrel{|}{\stackrel{|}{\rm C}} \stackrel{|}{-{\rm C-Cl}}, \\ {\rm CH_3\,H} \end{array}$$

Neohexyl chloride (1°)

Thus, (d) is a primary  $(1^{\circ})$  halide.

16. (a) 
$$X \xrightarrow{PCC} Y \xrightarrow{I_2/\text{alkali}} CHI_3$$
  
Compound Y must give iodoform test.  
Further since Y is obtained by the oxidation

of X which must be an alcohol ( $CH_3CH_2OH$ ) and thus Y is  $CH_3CHO$ .

17. (c) Ethanol on dehydration forms diethyl ether.

$$C_2H_5OH + HOC_2H_5 \longrightarrow C_2H_5OC_2H_5 + H_2O$$

**18.** (d) Chloropicrin is nitrochloroform. It is obtained by the nitration of chloroform with HNO<sub>3</sub>.

$$\begin{array}{ccc} \text{HCCl}_3 & \xrightarrow{\text{HNO}_3} & \text{O}_2\text{NCCl}_3 \\ \text{Chloroform} & & \text{Chloropicrin} \end{array}$$

Chloropicrin is a liquid, poisonous and used as an insecticide and in war gas.

**19. (b)** Heavy metal ions, particularly  $Ag^+$ , catalyse  $S_N^-1$  reaction because of presence of empty orbital.

$$CH_3CH_2Br + Ag^+$$

$$[CH_3CH_2 \dots Br \dots Ag]^+$$

$$\xrightarrow{\text{slow}} CH_3CH_2^+ \xrightarrow{\text{oH}^-} CH_3CH_2OH$$

- **20. (b)** Due to greater electronegativity of  $sp^2$ -hybridized carbon atoms of the benzene ring, diaryl ethers are not attacked by nucleophiles like  $I^-$ .
- **21. (a)** Hydroboration-oxidation leads to *anti-* Markownikoff's hydration, thus

22. (c) 
$$C_2H_5NO_2 \leftarrow AgNO_2 - C_2H_5OH \xrightarrow{PCl_5} C_2H_5Cl + POCl_3 + HCl$$
[A]

23. (b) Vinyl alcohol, CH<sub>2</sub>=CHOH, monomer of polyvinyl alcohol exists mainly as CH<sub>3</sub>CHO; hence polyvinyl alcohol is best prepared by the alkaline hydrolysis of polyvinyl acetate which in turn is prepared by the polymerisation of vinyl acetate.

#### c-158

- Topicwise AIIMS Solved Papers - CHEMISTRY

**24.** (a) Reaction involved is given as:

$$\begin{array}{c|cccc} CH_3 & CH_3 \\ & & & CH_3 \\ CH_3-C-OH & \xrightarrow{ZnCl_2} & CH_3-C-Cl \\ & & & CH_3 \\ CH_3 & & & CH_3 \\ (A) & & & (B) \end{array}$$

25. (d) 1-pentanol
Primary alcohols readily form ether when heated with conc. H<sub>2</sub>SO<sub>4</sub>.

26. (d) 
$$6CH_3-CH=CH_2 \xrightarrow{B_2H_6} \frac{B_2H_6}{\text{ether, 0°C}}$$

$$2(CH_3CH_2CH_2)_3B \xrightarrow{H_2O_2} OH^-$$

$$\begin{array}{c} 6\mathrm{CH_3CH_2CH_2OH} + 2\mathrm{H_3BO_3} \\ \mathrm{Propanol} \end{array}$$

27. (a)

28. (c) CICH<sub>2</sub>CH<sub>2</sub>OH is stronger acid than CH<sub>3</sub>CH<sub>2</sub>OH due to – I effect of Cl.

$$\begin{array}{c} \text{Cl} \longleftarrow \text{CH}_2\text{CH}_2\text{OH} \longrightarrow \text{Cl} \longleftarrow \text{CH}_2\text{CH}_2\text{O}^- + \text{H}^+ \\ \text{Stronger acid} & -\text{ve charge on O} \\ & \text{dispersed hence} \\ & \text{conjugate base, stable} \end{array}$$

$$CH_3CH_2OH \longrightarrow CH_3 \longrightarrow CH_2O^- + H^+$$
Weaker acid

-ve charge intensified,
hence conjugate
base unstable

29. (b)

**30.** (a) Since glycerol has three –OH groups, it can have three acyl (similar or different) groups

31. (d) 
$$NaOH$$
 OH

 $CO_2 + HCl$ 
 $ACOOH$ 

Salicylic acid

**32. (b)** 

Type B: Assertion Reason Questions

**33.** (a) Phenols turn FeCl<sub>3</sub> solution purple Resorcinol has phenolic group.

**34. (b)** Phenol is strong acid than ethanol because phenoxide ion is resonance stabilised. When a group having +M effect is at *p*-position (like halide group) it decreases the acidity of phenols. So assertion and reason are correct but reason is not the explanation of assertion. So correct option is (b).

**35. (c)** The reaction follows S<sub>N</sub>1 mechanism for two reasons :

$$C_6H_5CH_2Br \longrightarrow C_6H_5CH_2^+ + Br^-$$

1. C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub><sup>+</sup> is stablised by resonance.

2. Steric hinderance of phenyl group.

**36.** (a) As benzyl cation  $(C_6H_5CH_2^+)$  is more stable than methyl cation  $(CH_3^+)$ , so the product is  $C_6H_5CH_2I$  and  $CH_3OH$ 

**37.** (a) The given order of dehydration is correct due to following reasons.

 Alcohols leading to conjugated alkenes are dehydrated more readily.

(ii) 2-Cyclohexenol is dehydrated more easily than 3-cyclohexenol because the carbocation from the former is more stable than the latter.

$$\begin{array}{c}
\text{OH} \\
& \downarrow \\
\text{OH} \\
\text{OH} \\
& \downarrow \\
\text{OH} \\
& \downarrow \\
\text{(less stable)}
\end{array}$$

(iii) Phenol is not dehydrated due to its highly stable character due to resonance.

**38.** (a) Phenol is an effective germicide. Phenyl is a derivative of phenol, that's why it also has germicidal property.

**39. (b)** On using *ter*-butyl bromide and sodium ethoxide as reactants, the major product would be 2-methylpropene and ethanol (elimination reaction).

$$CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} CH_{3} \xrightarrow{CH_{3}} -CH_{2} \xrightarrow{CH_{3}} CH_{3}$$

**40.** (a) Ethers have lone pair on oxygen, so they behave as Lewis base. It forms salt known as oxonium salt with acids.

$$\begin{array}{c}
R \\
R
\end{array}$$

$$O: + H^{+}CI^{-} \longrightarrow \begin{bmatrix}
R \\
R
\end{array}$$

$$O^{+} - H$$

$$CI$$

**41.** (c) It is correct that sodium phenoxide (sodium salt of phenol) and  $CO_2$  on heating form

- sodium salicylate. This is known as Kolbe's reaction. Ethanol does not respond to this reaction. Therefore, Assertion is true. But the Reason that phenoxide ion is more basic than ethoxide ion is not correct.
- **42. (c)** Alkyl aryl ethers are cleaved at the alkyloxygen bond due to the more stable aryloxygen bond. The reaction yields phenol and alkyl halide

$$O - R \qquad OH$$

$$+ H - X \longrightarrow + R - X$$

Ethers with two different alkyl groups are also cleaved in the same manner.

$$R - O - R' + HX \rightarrow R - X + R' - OH$$